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TITLE : CLEANING OR ETCHING GAS

ABSTRACT : PURPOSE: To obtain a cleaning gas, comprising a perfluorocarbon containing a hetero-atom and capable of removing a metal, etc., deposited on an apparatus for forming a thin film in etching the thin film or a thick film formed according to a chemical vapor deposition(CVD), a sputtering, a sol-gel or a vapor deposition method.

CONSTITUTION: This cleaning gas comprises a perfluorocarbon containing a hetero-atom such as a perfluoroalkylamine, a perfluoroalkyl ether, a perfluoroalkyl ketone, a perfluoroalkylcarbonyl fluoride or a perfluoro cyclic ether. The cleaning gas is used to remove deposits in etching a thin or a thick film, formed with an apparatus for forming the thin film and comprising a metal or its compound, cutting an ingot or polishing a surface.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] this invention relates to the cleaning gas for removing the unnecessary sediment deposited on the equipment wall, the \*\* implement, etc. in the equipment which manufactures the etching gas for carrying out etching of the thin film which formed membranes using CVD, the sputtering method, the sol gel process, and the vacuum deposition, and a thick film or a disconnection of an ingot, and surface polishing and a thin film, a thick film, fine particles, and a whisker.

#### [0002]

[The conventional technique and its trouble which it is going to solve] In a thin film device manufacture process and the charge manufacture process of super-steel materials centering on semiconductor industry, various thin films, a thick film, fine particles, and the whisker are manufactured using CVD, the sputtering method, the sol gel process, and the vacuum deposition. In case these are manufactured, a sediment generates to the \*\* implement which supports a layer, a whisker, reactor walls other than on fine particles should be made to deposit on ] the specified substance, and the specified substance. Since it will become the cause of particle occurrence and it will become difficult to manufacture a good layer, grain, and a whisker if an unnecessary sediment generates, you have to remove at any time. Moreover, in order to form a circuit pattern in various kinds of thin film materials which constitute a circuit in a semiconductor, TFT, etc., it is necessary to perform vapor etching which removes a thin film material partially. Furthermore, in CVM (chemical \*\*\*\*\* permanent wave \*\*\*\*\*), vapor etching needs to cut Si ingot etc.

[0003] \*\* with comparatively easy processing of \*\* exhaust gas that the reaction rate to \*\* etching or a cleaning object is quick as a performance for which the etching gas which removes such an unnecessary sediment or cuts a material, and cleaning gas are asked -- influence of as opposed to [ it is comparatively unstable in the atmospheric air, and ] global warming -- the parvus -- things and a grade are desired In order to etch elimination and layer material of such an unnecessary sediment in the present condition, they are C2 F6 and CF4. The gas of a grade is used. However, these gas is very stable compounds, processing of the exhaust gas after cleaning or etching is difficult, and since an elevated temperature is needed for processing, a running cost becomes comparatively high. Furthermore, the catabolic rate in the inside of the atmospheric air is late long lasting, and it exists stably in an environment, and since a global-warming coefficient is high, the bad influence to an environment poses the problem.

#### [0004]

[The concrete means for solving a trouble] Zealously, as a result of a study, this invention persons find out the cleaning gas for removing efficiently the unnecessary sediment deposited on the equipment wall, the \*\* implement, etc. in the equipment which manufactures the etching gas for carrying out etching of the thin film which formed membranes using CVD, the sputtering method, the sol gel process, and the vacuum deposition, and a thick film or a disconnection of an ingot, and surface polishing and a thin film, a thick film, fine particles, and a whisker, and reach this invention.

[0005] That is, this invention is CF4 and C2 F6. It is easy to dissociate rather than a grade, and when the catabolic rate in the inside of the atmospheric air uses the gas containing the perfluoro carbon containing the hetero atom with few [ it is quick and ] bad influences to earth environment comparatively easily [ an offgas treatment ], the cleaning gas for removing the unnecessary sediment which deposited a thin film, a thick film, etc. which formed membranes in the etching gas for etching and equipment is offered.

[0006] The matter with which this invention should perform target etching or cleaning is B, P, W, Si, Ti, V, Nb, Ta, Se, Te, Mo, Re, Os, Ir, Sb, germanium, Au, Ag, As, Cr, and its compound, and is specifically an oxide, a nitride, carbide, and these alloys.

[0007] Moreover, the etching gas or cleaning gas in this invention 3 N [tri-trifluoromethylamine], (CF3) 3 N [tri-pentafluoroethylamine], (C2 F5) 3 N [tri-heptafluoropropylamine], (C3 F7) C6 F11NF2 [tridecafluorocyclohexylamine], C5 F10NF [undecafluoropiperidine], 2 NC3 F7 [N and N-di-pentafluoroethyl-heptafluoropropylamine], (C2 F5) (i-C3 F7) 2 NC2 F5 [N and N-di-heptafluoroisopropyl-pentafluoroethylamine], CF3 OCF3 [di-trifluoromethyl ether], C2 F5 OC2 F5 [di-pentafluoroethyl ether], C3 F7 OC3 F7 [di-heptafluoropropylether], C4 F9 OC4 F9 [di-nonafluorobutylether], C4 F9 OCF3 [nonafluorobutyl-trifluoromethyl ether], CF3 OCF2 CF2 OCF3 [decafluoro-glycol dimethyl ether], C6 F11OCF3 [undecafluorocyclohexyl-trifluoromethyl ether], C4 F8 O [octafluorotetramethylene oxide], C5 F10O [decafluoropentamethylene oxide], CF3 COF [trifluoroacethyl fluoride], C2 F5 COF [pentafluoropropionyl fluoride] C3 F7 COF [heptafluorobutyl fluoride] and CF3 COCF3 [hexafluoroacetone] etc. is mentioned. 3 (CF3) N, CF3 OCF3, CF3 COCF3, CF3 COF, and C4 F8 O is mentioned especially preferably.

[0008] In consideration of the modality of material currently used for the equipment which manufactures a modality, thickness, a thin film, etc. of the sediment which should be removed, the perfluoro carbon containing a hetero atom itself is used, or the cleaning gas in this invention is inert gas, such as nitrogen, an argon, and helium, H<sub>2</sub> and O<sub>2</sub>, F<sub>2</sub>, ClF<sub>3</sub>, BrF<sub>3</sub>, and BrF<sub>5</sub>. What is necessary is to dilute with a grade, and to use or just to choose suitably. Moreover, it is not restricted, especially concerning a reaction condition and is suitably chosen in consideration of an object material as above-mentioned.

[0009] Moreover, in consideration of the modality of layer which formed membranes, thickness, etc., the perfluoro carbon containing a hetero atom itself is used, or the etching gas in this invention is inert gas, such as nitrogen, an argon, and helium, H<sub>2</sub> and O<sub>2</sub>, F<sub>2</sub>, ClF<sub>3</sub>, and BrF<sub>3</sub> and BrF<sub>5</sub>. What is necessary is to dilute with a grade, and to use or just to choose suitably. Moreover, it is not restricted, especially concerning a reaction condition and is suitably chosen in consideration of an object material as above-mentioned.

[0010]

[Example] Hereafter, although an example explains this invention in detail, it is not limited to such an example.

[0011] The test piece which made 20 micrometers of silicon oxides deposit on a silicon wafer (4 inches) in a sol gel process was created, respectively, having used as the main raw material the test piece which made 20 micrometers of silicon oxides deposit on a silicon wafer (4 inches), and the tetraethyl orthochromatic silicate using parallel monotonous type plasma CVD equipment having used examples 1-4, the example 1 of a comparison, - 2 tetraethyl orthochromatic silicate as the main raw material. These test pieces are installed on the lower electrode of plasma CVD equipment, and they are 3 (CF<sub>3</sub>) N, CF<sub>3</sub> OCF<sub>3</sub>, and C<sub>2</sub> F<sub>6</sub>. \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed the test piece for three sorts of gas under gas pressure 1Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, and etching was performed. The measurement result of these etch rates was shown in Table 1.

[0012]

[Table 1]

	成膜法	ガス種	エッティング速度
実施例1	CVD法	(CF <sub>3</sub> ) <sub>2</sub> N	4890 A/min
実施例2	ゾルゲル法	(CF <sub>3</sub> ) <sub>2</sub> N	6280 A/min
実施例3	CVD法	CF <sub>3</sub> OCF <sub>3</sub>	4650 A/min
実施例4	ゾルゲル法	CF <sub>3</sub> OCF <sub>3</sub>	5720 A/min
比較例1	CVD法	C <sub>2</sub> F <sub>6</sub>	2360 A/min
比較例2	ゾルゲル法	C <sub>2</sub> F <sub>6</sub>	3890 A/min

[0013] Examples 5-6 and example of comparison 3 silicon wafer is installed on the electrode of a CVD system, and they are 3 (CF<sub>3</sub>) N, CF<sub>3</sub> OCF<sub>3</sub>, and C<sub>2</sub> F<sub>6</sub>. Three sorts of gas under gas pressure 760Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature \*\*\*\* (the RF-generator frequency of 13.56MHz, 2mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed the test piece, and etching was performed. The measurement result of these etch rates was shown in Table 2.

[0014]

[Table 2]

	ガス種	エッティング速度
実施例5	(CF <sub>3</sub> ) <sub>2</sub> N	25.4 μm/min
実施例6	CF <sub>3</sub> OCF <sub>3</sub>	24.6 μm/min
比較例3	C <sub>2</sub> F <sub>6</sub>	19.3 A/min

[0015] They are W layer, WSi layer, TiC layer, and Ta<sub>2</sub> O<sub>5</sub> with seven to example 8 heat CVD. 50 micrometers of layers were formed on the nickel substrate (L10mmxD20mmx12mm). \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed these four sorts of test pieces on the lower electrode of plasma CVD equipment, and installed the test piece for 3 (CF<sub>3</sub>) N and two sorts of gas of CF<sub>3</sub> OCF<sub>3</sub> under gas pressure 1Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, and cleaning was performed for 20 minutes. Then, when the test piece was taken out from the inside of a CVD system and having been analyzed by the electron probe X-ray microanalyser, the peak of W, Si, and Ti did not accept.

[0016] Mo layer, Re layer, and 50 micrometers of Nb layers were formed on the nickel substrate (L10mmxD20mmx12mm) with nine to example 10 heat CVD. These three sorts of test pieces are installed on the lower electrode of plasma CVD equipment, and they are 3 (CF<sub>3</sub>) N and CF<sub>3</sub> OCF<sub>3</sub>. \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed the test piece for two sorts of gas

under gas pressure 1Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, and cleaning was performed for 20 minutes. Then, when the test piece was taken out from the inside of a CVD system and having been analyzed by the electron probe X-ray microanalyser, the peak of Mo, Re, and Nb did not accept.

[0017] TiN layer and 5 micrometers of Ti layers were formed on the nickel substrate (L10mmxD20mmxt2mm) by 11 to example 12 sputtering. These two sorts of test pieces are installed on the lower electrode of plasma CVD equipment, and they are 3 (CF3) N and CF3 OCF3. \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed the test piece for two sorts of gas under gas pressure 1Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, and cleaning was performed for 10 minutes. Then, when the test piece was taken out from the inside of a CVD system and having been analyzed by the electron probe X-ray microanalyser, the peak of Ti did not accept.

[0018] Au layer, Ag layer, and 2 micrometers of Cr layers were formed on the nickel substrate (L10mmxD20mmxt2mm) with 13 to example 14 vacuum deposition. These three sorts of test pieces are installed on the lower electrode of plasma CVD equipment, and they are 3 (CF3) N and CF3 OCF3. \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed the test piece for two sorts of gas under gas pressure 1Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, and cleaning was performed for 10 minutes. Then, when the test piece was taken out from the inside of a CVD system and having been analyzed by the electron probe X-ray microanalyser, the peak of Au, Ag, and Cr did not accept.

[0019] In the boat made from 15 to example 16 nickel, P, Ta, As, germanium, Se, It takes 5mg of the fine particles of B at a time, a boat is installed on the lower electrode of plasma CVD equipment, and they are 3 (CF3) N and CF3 OCF3. Two sorts of gas under gas pressure 1Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature Although the inside of a boat and equipment was observed after having carried out \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power to the lower electrode which installed the test sample and cleaning for 10 minutes, fine particles had carried out gasification elimination.

[0020] 120 micrometers of silicon were formed on the glass substrate (L100mmxD100mmxt2mm) by examples 17-18 and example of comparison 4 plasma CVD. At this time, a lot of layers had accumulated also on an equipment wall, a lower electrode, and the outskirts of an up electrode. The glass substrate on which silicon was made to deposit is installed on an up electrode, and they are 3 (CF3) N, CF3 OCF3, and C2 F6. Under gas pressure 5Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode, and three sorts of gas was cleaned for 120 minutes The result which observed a glass substrate and the interior of a reactor was shown in Table 3 after the cleaning end.

[0021]

[Table 3]

	ガス種	観察結果
実施例17	(CF <sub>3</sub> ) <sub>3</sub> N	硝子基板上及び反応器内部のシリコンが完全に除去されていた。
実施例18	CF <sub>3</sub> OCF <sub>3</sub>	硝子基板上及び反応器内部のシリコンが完全に除去されていた。
比較例4	C <sub>2</sub> F <sub>6</sub>	硝子基板上のシリコンは完全に除去されていたが反応器側壁部のシリコンは完全には除去されなかった。

[0022] 60 micrometers of silicon nitrides were formed on the glass substrate (L100mmxD100mmxt2mm) by examples 19-20 and example of comparison 5 plasma CVD. At this time, a lot of layers had accumulated also on an equipment wall, a lower electrode, and the outskirts of an up electrode. The glass substrate on which the silicon nitride was made to deposit is installed on an up electrode, and they are 3 (CF3) N, CF3 OCF3, and C2 F6. Under pressure 5Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature, \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode, and three sorts of gas was cleaned for 120 The result which observed a glass substrate and the interior of a reactor was shown in Table 4 after the cleaning end.

[0023]

[Table 4]

	ガス種	観察結果
実施例19	(CF <sub>3</sub> ) <sub>2</sub> N	硝子基板上及び反応器内部の窒化シリコンが完全に除去されていた。
実施例20	CF <sub>3</sub> OCF <sub>3</sub>	硝子基板上及び反応器内部の窒化シリコンが完全に除去されていた。
比較例5	C <sub>2</sub> F <sub>6</sub>	硝子基板上の堆積物は完全に除去されていたが反応器側壁部の堆積物は完全には除去されなかった。

[0024] The test piece which made 20 micrometers of silicon oxides deposit on a silicon wafer (4 inches) was created using parallel monotonous type plasma CVD equipment, having used examples 21-25 and the example of comparison 6 tetraethyl orthochromatic silicate as the main raw material. These test pieces are installed on the lower electrode of plasma CVD equipment. 3 N, CF<sub>3</sub>OCF<sub>3</sub>, CF<sub>3</sub>COCF<sub>3</sub>, and C<sub>4</sub>F<sub>8</sub>O, (CF<sub>3</sub>)<sub>2</sub>COF and C<sub>2</sub>F<sub>6</sub> Six sorts of gas is diluted with helium to 10vol% under gas pressure 10Torr, quantity-of-gas-flow 100SCCM, and the condition of a room temperature \*\*\*\* (the RF-generator frequency of 13.56MHz, 50mm of \*\*\*\* 0.315W [cm] power 2 and inter-electrode distance) of the RF power was carried out to the lower electrode which installed the test piece, and etching was performed. The measurement result of these etch rates was shown in Table 5.

[0025]

[Table 5]

	成膜法	ガス種	エッチング速度
実施例21	CVD法	(CF <sub>3</sub> ) <sub>2</sub> N +He	5240A/min
実施例22	CVD法	CF <sub>3</sub> OCF <sub>3</sub> +He	4940A/min
実施例23	CVD法	CF <sub>3</sub> COCF <sub>3</sub> +He	5110A/min
実施例24	CVD法	C <sub>4</sub> F <sub>8</sub> O +He	5620A/min
実施例25	CVD法	CF <sub>3</sub> COF +He	4150A/min
比較例6	CVD法	C <sub>2</sub> F <sub>6</sub> +He	2680A/min

[0026]

[Effect of the Invention] The cleaning gas of this invention and etching gas show the extremely excellent etching performance.

[Translation done.]